academicJournals

Vol. 10(12), pp. 451-466, December 2016
DOI: 10.5897/AJEST2016.2203
Article Number: F72C4A961553
ISSN 1996-0786

http://www.academicjournals.org/AJEST

African Journal of Environmental Science and Technology

Review

Hydrogeochemical and isotopic characterization of the groundwater in the Dababa area (Chad)

Abderamane H.[1*], Ketchemen-Tandia B.[2], Nlend B. Y.[2] and Arrakhais A. B.[2]

[1]University of N'djamena, Faculty of Exact and Applied Sciences, Department of Geology, POB 1027, N'djamena, Chad.
[2]University of Douala, Faculty of Sciences, Department of Earth Sciences, POB 14157, Douala, Cameroon.

Received 11 September, 2016; Accepted 21 October, 2016

The Central-African country of Chad, located in the Sahel-Sahara zone, faces diverse shortages of portable water. The only reliable source of water available for drinking, domestic and agricultural use in the Dababa Division is groundwater. Conventional hydro-geochemical and isotopic methodology, coupled with piezometric data, allowed investigators to identify the numerous process affecting not only water quality, but also aided them to assess its suitability for different uses. The types of groundwater encountered indicated the presence of Ca-Mg-HCO_3, Na-HCO_3, Cl-SO_4 and Na-Ca-SO_4 in descending order of abundance. The data presented in this investigation shows three processes influenced the groundwater quality; these are the alteration of silicate minerals by dissolved CO_2, the cationic exchange and the evaporation phenomenon, in particular, in the piezometric depression. Additionally, to these findings, this article discussed the anthropogenic processes involved, whose effects are evident in many samples with nitrate concentrations above the WHO standards. Generally, the groundwater in the study area show signs of human contamination. Recent studies also indicate the development of cardiovascular diseases among the population of this area which are directly linked to the low total hardness (TH) values, or general softness, of the water. The groundwater in Dababa is, however, usable for agricultural and other domestic needs. Based on the calculation of Na‰ and the sodium adsorption ratio, the sampled waters are suitable for irrigation.

Key words: Groundwater, World Health Organization (WHO), hydrogeochemistry, isotope, Dababa, Chad.

INTRODUCTION

Access to clean water is one of the greatest concerns for all humanity. African governments, in general and Chad in particular are striving to provide their people with portable water. In the Dababa area, groundwater is the main source of drinking water and is very important in agro-pastoral activities, because of the scarcity of rainfall and hence surface water. Given that access to potable water for both human consumption and agriculture is

*Corresponding author. E-mail: abderamanehamit@gmail.com.

essential to the development of a country, a better understanding of the origin and mechanisms for qualitative and quantitative water degradation will contribute to sustainable water management. Thus, an effective qualitative and quantitative management of groundwater resources is needed which requires a good understanding of how the reservoir functions. This knowledge includes the contribution of water found in arid areas where a decline of rainfall influences the ground-water recharge. In the Dababa region in Central Chad, the groundwater resource is located in the Quaternary (Lower Pleistocene) and Tertiary (Lower Pliocene). The Quaternary shallow water contributes >80% of drinking water and irrigation needs in the region (CBLT/BGR, 2012). This aquifer can be seen as exploitative and hazardous without any qualitative and quantitative monitoring. Abderamane (2012) and CBLT/BGR (2013) noted a considerable drop in groundwater levels and quality in the Chari-Baguirmi basin. However, the current level of understanding of the Dababa aquifer system-ESE of the Lake Chad basin is very limited. The water mineralization process of the whole area, as well as the flow direction of the water and its relationship with the surface water are unknown. The data herein is the result of the first hydrogeological investigation in the study area (8182.92 km^2) home to 219,686 people, where agriculture and animal husbandry is the main economic activities (INSEED, 2012). The aim of this study is therefore to contribute to the knowledge of the functioning of aquifer system in relation to surface water in the investigated area, as well as, suggesting methods for the protection of groundwater resources.

With the aid instruments conventionally used in hydrochemistry, we firstly characterized the chemical faces of shallow groundwater to create an understanding of the water mineralization process. This helped us to establish not only water-rock interactions, but also determine areas of recharge and discharge. Secondly, using hydro-chemical experiments, we established the degree of portability of water to show the possible use in irrigation which aided us to assess the impact of human activities on the groundwater. Lastly, we applied geochemical and isotopic methods to investigate hydrogeological problems in semi-arid regions to get information on environmental issues and social development in the rural areas.

LOCATION AND CLIMATOLOGY OF STUDY AREA

The study area 8182,92 km^2 (Figure 1) is located between latitudes 11.70 and 12.60° North and longitudes 16.5 and 17.60° East. It is bounded to the south by the Chari River and to the west by the Lake Chad region.

The climate fluctuates between semi-arid and arid. The rainfall in this region is very irregular and influenced by the movement of the Inter-Tropical Convergence Zone (ITCZ), which is in turn controlled by two major wind systems, the NE Trade winds (or the Harmatan; hot and dry wind blowing from the high pressure zone in Saharan) and the SW Monsoons (cool and moist wind from the Atlantic Ocean). The annual rainfall of the area is also affected by the relief, while the southward shift of the isohyets in the Lake Chad basin is due to Adamawa Massif and Yadé that disrupt the advance of the monsoon towards Chad as a whole. Data from 30 years worth of observation in the Bokoro station (located in the centre of the study area) show an annual average rainfall of 542 mm with the peak of the data in August reaching 189 mm. Twenty years accumulation of records of temperatures show ranges between 15 and 41°C with an average of 28°C per year. December and January are the coolest months, while April and May are the hottest. The relative humidity of the air shows an annual change of 25 to 47% (1965 to 1995) with a mean of 36%. Olivry (1986) observed more than twice this value in Douala (Cameroon); which has an equatorial climate with a unimodal distribution pattern of monthly rainfall.

GEOLOGIC AND HYDRO-GEOLOGIC SETTINGS

Chad belongs to a large post-Palaeozoic sedimentary basin which is extended up to Niger, Nigeria and Cameroon. The sediments lie unconformably on the Palaeozoic or Achaean and Proterozoic sediments (Kusnir, 1995). The basement level of the study area includes the crystalline formations overlain by sedimentary formations. The base is flush with inselbergs such as Moyto, Kalkalé, Andreieb and Hadjer Terchap (Figure 1). It consists of late-tectonic alkaline granites, rhyolites, diorites and dolorites (Blanchot and Muller, 1973). Neogene hyperalkaline rhyolites, located on the same volcanic axis, are also contemporary to those encountered in Cameroon and Tibesti (Barbeau and Gese, 1957).

The thickness of the post-Paleozoic sedimentary fill varies from place to place; from several thousand meters in the grabens (Louis, 1970) formed during the Early Cretaceous period (Maurin and Guiraud, 1993) to less than 1000 m. Cretaceous sediments are mainly continental, except in places where the sea levels had risen during the Upper Cretaceous period following the transgressions in the Upper Cenomanian-Turonian and Maastrichtian Lower Paleocene-Terminals (Bellion, 1989).

The Cenozoic or Continental Terminal (CT) corresponds to fluvial and lacustrine sediments interbedded with sandy-clay to ferruginous horizons with intercalations of oolites and ferruginous armors (Moussa, 2010). These formations, which are the result of the weathering of crystalline rocks, attain a thickness of 200 m in the centre

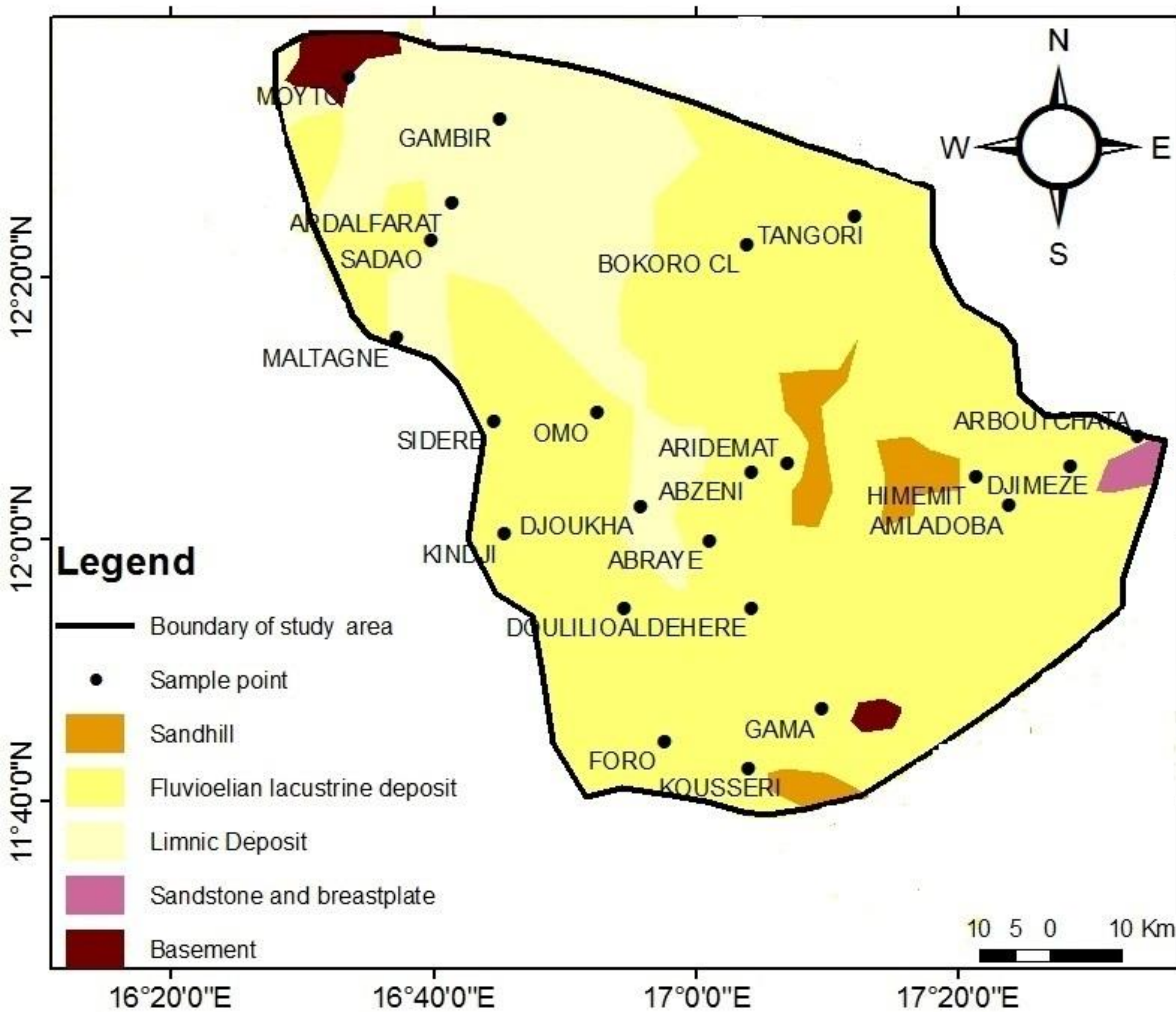

Figure 1. Location and geology of the Dababa area showing groundwater samples points.

of the basin.

At the upstream level of the Continental Cenozoic, lie unconformably the Pliocene and the Quaternary formations made up of discontinuous layers of varying thickness of lacustrine clays and altered limnic sands. The stratigraphic boundary between the Pliocene and Quaternary is not clear. Schneider (1989) proposed two types of limits: (i) the conventional limit corresponding to 1.8 Ma and (ii) the episodic palaeomagnetic Olduwai. The second is chosen because of its practicality and of its distinctive quality on the logs (Schneider and Wolf, 1992). However, Pliocene clay sedimentation (aquifer wall) marked the end of Quaternary and the beginning of the sedimentation of sand and clay deposits. The origin of these sediments, fluvial, lacustrine and deltaic, explains the rapid variation of the faces, laterally and vertically. These Pliocene and Quaternary sands still contain water. These multi-layered aquifers are captured in the Pliocene and locally communicate freely with the semi-Quaternary through leakages.

The shallow groundwater of the Dababa locality flows in the formations of the lower Pleistocene (UNDP/UN, 2002). At the eastern boundary of the zone, the water flows on the North Continental Terminal Formations. This aquifer extends northward to the Kanem region (which has wind sand) and southward into the Mayo Kebbi (Southern Continental Terminal). It is bordered to the southeast and east by the Pliocene formations. The depth of this aquifer varies from 35 to 75 m and furnishes all the wells drilled in this area (Leblanc, 2002). The shallow groundwater is recharged mainly by precipitation and to a lesser extent by the exfiltration of the deeper aquifers (Schneider, 2001). During the rainy season, rainfall and over-flooding rivers that build up in the

Table 1. Sedimentary formations and aquifers in Dababa.

Stratigraphics units		Aquifer sand non aquifers	Thickness
Quaternary	Holocene	Permeable roof	-
	Pleistocene	Shallow groundwater of sand	35 to 75 m
Neogene	Upper Pliocene	Sandy clays Sandy aquifer	80 to 145 m
	Middle Pliocene	Limnic clays with sandy intercalations	
	Lower Pliocene	Sandy aquifer	
Paleo-Neogene	Oligo-Miocene	Breast plate Aquifer of Continental Terminal (CT)	<10 m

backwaters and floodplains, give rise to temporary water courses that contribute to the groundwater recharge (Djoret, 2000). The lower Pliocene contains a confined aquifer beneath the Middle Pliocene clay sequences with a thickness that varies from 80 to 145 m with an average permeability (Schneider, 2001). The extreme depth and low productivity of this water reserve make it difficult to exploit. Together with the lower Pliocene and the Quaternary formations, an important multi-layered aquifer is established which has an estimated water reserve of 206 billion or 94.6 m^3 with a renewable volume of ~3600 million m^3 in Chari-Baguirmi (Abderamane, 2012). Schneider and Wolf (1992) also reported resources related to granitic massifs which are in the form of (i) fissured aquifers related to the direct infiltration of rainwater and runoff on mountains slopes and (ii) water contained in arenas from the breakdown of granite Massifs, with their substratum consisting of the bedrock, for example in the case of Moyto. Table 1 shows the stratigraphy and hydro-geological formations in the Dababa area.

SAMPLE COLLECTION AND ANALYSIS

In July 2015, which marks the beginning of the rainy season, twenty-three wells were sampled in the west-central part of the country. Water samples were collected in polyethylene bottles of 0.5 L with all necessary precautions. The samples were collected in a sedimentary (22 samples) and basement (01 sample) levels. Figure 1 shows all the sampled points. Their spatial distribution depended on the geographic location of the selected villages. The pH, electric conductivity (EC) and temperature of each sample was measured in the field using multi-WTW device parameters. Besides these measurements, the static levels were taken individually in each well by means of a potentiometric sensor. Latitude and longitude were also determined on the field using the GPS.

Major ions were analyzed in the “Laboratoire National d’Analyse des Eaux” in N'Djamena-Chad. Results show the major ions: Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-} and NO_3^-. The concentration of Na^+ and K^+ was determined by flame photometry, Ca^{2+} by titration and Mg^{2+} by subtraction between certain compounds. The contents of HCO_3^- and Cl^- were also measured by titration and those of NO_3^- and SO_4^{2-} using the DR2800 Spectro-photometer. Samples were filtered through 0.2 µm filters before the various analyses. The analytical precision of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) was checked through the ionic balance error (IBE) based on ions concentrations expressed in meq/L (Appelo and Postma, 1999). All the investigated points gave an IBE value of ±5%. The equipment and instruments were tested and calibrated using standard calibration methods as described in APHA et al. (1998). Total Dissolved Solids (TDS) were calculated by adding the main ionic species (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-).

The isotopes 18O and 2H (Deuterium) were analyzed in Leibniz Institut for Applied Geophysics Laboratory (Hannover, Germany). Water samples were analyzed for δ2H using a fully automated chromium reduction system at 800°C (H/Device, Thermo Finnigan) directly coupled to the dual inlet system of Thermo Finnigan Delta XP isotope ratio mass spectrometer. Water samples were analyzed for δ18O using an automated equilibration unit (Gasbench 2, Thermo Finnigan) in continuous flow mode. All samples were measured at least in duplicates and the reported value is the mean value. All values are given in the standard delta notation in permill (‰) versus VSMOW according to $\delta[‰] = [R_{sample} / R_{reference} - 1] \times 1{,}000$.

RESULTS AND DISCUSSION

Summary statistics

Table 2 is a presentation of a summary statistic of physico-chemical and chemical parameters analyzed in

Table 2. Summary data of physico-chemical and chemical parameters of groundwater (n=23) in the Dababa area.

Parameter	Min.	Max.	Median	SD	Mean
pH	6.3	7.7	6.87	0.36	6.9
EC (µs/cm)	61	2900	181	647.59	474
Temp (°c)	27.4	33.5	30.95	1.64	30.69
TDS (mg/L)	54.95	2138.5	152.03	478.44	364.73
Ca^{2+} (meq/L)	0.12	7.75	0.7	1.4	1.7
Mg^{2+} (meq/L)	0.2	3.11	0.3	0.5	0.6
Na^{+} (meq/L)	0.17	20.26	0.6	2.8	2.3
K^{+} (meq/L)	0.06	1.02	0.2	0.2	0.3
Cl^{-} (meq/L)	0.02	7.46	0.2	0.8	0.6
NO_3^{-} (meq/L)	0.00	4.48	0.11	1.05	0.49
SO_4^{2-} (meq/L)	0.01	17.92	0.1	2	1.3
HCO_3^{-} (meq/L)	0.34	7.2	1.4	1.7	2.4
%Na	24.80	74	38.42	12.61	42.53
SAR	0.33	9.18	0.64	2.65	1.77

this study. The median distribution descriptor is much more robust than the average values, the findings will be used here as the main statistical descriptor. The pH values are between 6.3 and 7.7 with a median of 6.87, indicating that waters are generally weakly acidic to neutral; and that the dissolved carbonates are predominantly in the HCO_3form (Adams et al*.,* 2001). The temperatures fall between 27.4 and 33.5°C with a mean of 30.95°C. The relatively high temperatures suggest a slow infiltration and shallow groundwater flow. The chemical composition of the Dababa groundwater shows a wide range of variation with a TDS of 54.95 to 2138.5 mg/L. However, the standard deviation values for each ion are low except for the nitrate ion. The low standard deviation values are explained by groundwater flow in a homogeneous geological environment, which is contributing to the chemistry of the water. The heterogeneity observed for NO_3 can be explained by the impact of the localized human pollution. The TDS values below 600 mg/L indicate that the groundwater is generally fresh. It also shows that it is weakly mineralized (Davis and De Wiest, 1966; Freeze and Cherry, 1979). The low values of TDS indeed correspond to groundwater silicate domain sand; this can be attributed to the slow dissolution rates of most silicate minerals (Appelo and Postma, 1999).

Calcium was found to be the dominant cation, which has an average concentration of 0.7 meq/L, followed by the Na+ with a mean concentration of 0.6 meq/L. Mg^{2+} and K^{+} respectively have a mean concentration of 0.3 and 0.2 meq/L. The HCO_3^{-} ion is the most dominant anion with a mean concentration of 1.4 meq/L, Cl^{-}(0.2 meq/L), NO_3^{-} (0.11 meq/L) and SO_4^{2-} (0.1 meq/L).

Dababa's groundwater seems to be affected by human activities as shown in the NO_3^{-} concentrations (Table 4) compared with WHO standards (10 mg/L). However, the water-rock interaction appears to be the major geochemical process responsible for the chemical quality of water.

Piezometry and spatial variation of the electrical conductivity

Depending on the availability and distribution of water points in the region, piezometric measurements were conducted in July 2015. The piezometric map (Figure 2) made using ArcGIS 10.2Software, enabled us to identify the following recharge areas: (i) two recharge areas to NW and (ii) three recharge areas in the S, SE and SW. The map also shows a current axis coinciding with the bed of the Batha de Lairi River. The hydraulic gradient of the southern and the north-western areas is quite high, indicating a high flow rate and low transmissivity of the aquifer. The electric conductivity ranges from 61 to 2900 µS/cm, in relation to the total dissolved solids contents (54.95 to 2138.5 mg/L). The spatial distribution map of the electrical conductivity of water from shallow groundwater of Dababa (Figure 2) shows that the highest conductivities are found in the discharge areas NW and NNE. Water mineralization generally increases from south to north. This geochemical evolution appears to be related to water-rock interaction. It may be the residence time of water in the aquifer which contribute to the mineralization and hence to the increased conductivity values. The well of Ardelfarat is characterized by a particular mineralization (EC = 2900 µS/cm). This can be explained by its location in the pastoral zone with a poor drainage system around the sample point, or it may be explained by the simple fact that it is in a piezometric

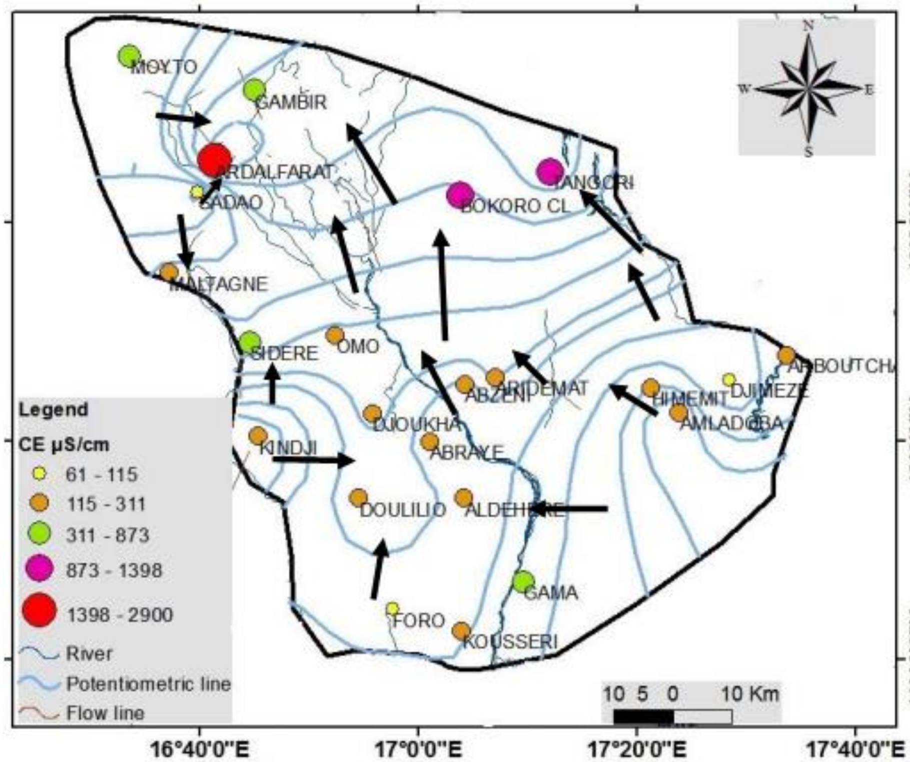

Figure 2. Piezometric map of Dababa associated with the spatial distribution of the electrical conductivity of shallow groundwater.

depression point of groundwater discharge. Lower values located in recharge areas can also be explained by dilution with infiltrated rainwater.

Major ion geochemistry

To classify groundwater of Dababa in west-central Chad and identify the geochemical processes, the piper diagram was used (Figure 3) (Piper, 1944). Diagrams software was used to represent the samples in the Piper and Riverside (Simler, 2007). This diagram shows that 66% of samples have Ca-Mg bicarbonate facies, 17% are of type Na-HCO_3, 13% are of type Cl-SO_4-Ca, and 4% have a $NaSO_4$ faces. $Ca(HCO_3)_2$ type characterized immature sedimentary waters of this aquifer. This type of water is found in almost all the waters of the area with a variable mineralization ranging from South to North of 61 to 457 µS/cm.

Sodium bicarbonate water types are found in the areas around the depressions and close to recharge area (Figure 4). The mineralization of these waters is very variable with values between 150 and 1324 µS/cm. The Piper diagram plot shows that the majority of calcium bicarbonate water types shift towards sodium bicarbonate water type end.

Na-SO_4 and Cl-SO_4-Ca types also noted by Abderamane (2012) in groundwater of Chari-Baguirmi, are mainly observed in the Ardalfarat (EC = 2900 µS/cm) depression, at the granitic intrusions and around the depression (172 µS/cm ≤ EC ≤ 1398 S/cm).

It is widely accepted today that each major ion dissolved in groundwater comes from three possible sources: (i) rain water, (ii) water-soil and water-rock interactions, and (iii) anthropogenic influences (Dafny et al., 2006).

In Figure 5, the relatively high concentration of chlorides zones correspond to high electrical conductivity. We distinguished (i) a southern sector with values ≤110 mg/L, which indicated an increase in southern content to the centre of the depression; (ii) the area of depression with values >110 mg/L. These high levels may have an explanation in the influence of evaporation phenomenon experienced by most hollow aquifers of Sahelian Africa (Coudrain-Ribstein et al., 1998).

The analysis of the map of sulphate contents (Figure 5) shows that it could be superimposed on a map of the electrical conductivities and the spatial distribution of the contents, which are not homogeneous in nature. As shown on the map, the lower levels are observed in the

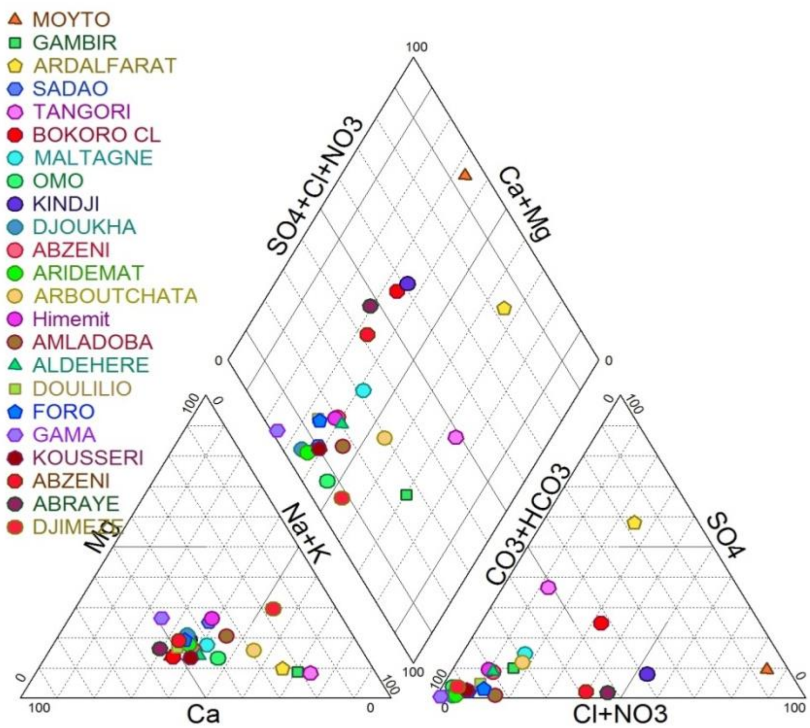

Figure 3. Chemical faces of groundwater in Dababa.

southern area of the depression in which they are less than 100 mg/L. There is also a gradual increase toward the centre of the depression. In addition, high concentrations in sulphates are also reported in Tangori, northwest of the study area, where besides the evaporation phenomenon which applies to the study area, an anthropogenic pollution is added. The highest value of bicarbonate is observed in north, and specifically in the north-eastern part, of the study region. The distributions of bicarbonate values do not seem to show any correlation with other elements. Calcium concentrations reach the maximum values of 150 and 155 mg/L in the wells of Bokoro and Ardalfarat, either at the centre or around the depression. These high levels suggest a Ca intake, either by evaporation phenomena, or by alteration of silicate minerals (e.g. feldspath).

Furthermore, the low concentrations can also be explained by a mineralization process such as cationic exchange (Figure 6). The spatial distribution of the K^+ is very heterogeneous. The highest concentration is at the base of outcrops and could have come from the alteration of rocks containing feldspath. The map of Na^+ contents (Figure 7) shows that the highest concentrations are observed in the region of the piezometric depression. These high values could have resulted from evaporation in the shallow groundwater. On the other hand, the lowest values are observed in the rest of the study area where groundwater is at the beginning of their migration towards the depression, that is, they have not yet undergone significant water rock interactions (Demlie et al., 2007). However, during the flow they might have gone through clay layers which are the basis of cation exchange. This phenomenon results from the fixing of Ca^{2+} after the release of two Na^+ or vice versa. The Mg contents could be explained by a similar process to that of Ca^{2+} ions described earlier. In short, Mg behaves in much the same manner as the calcium in the aquifer. The analysis of the map of nitrate levels (Figure 5) indicates that the spatial distribution of contents is not homogeneous. Examination of this map clearly shows highlighted areas polluted by nitrates (>50 mg/L) in the north of the study area. The presence of nitrates in these agro-pastoral areas owes its origin to an explanation related to redox reactions of organic materials associated with human activities or animal and vegetable production. Indeed, the long stay of livestock waste at the edges of water sources, the transport of these by droppings sump rope are the basic elements of the aquifer pollution. Additionally, a significant portion of the water flowing out of the trough around the wells, thus constituting quasi-permanent puddles that are enriched in nitrates from cattle dung left during watering (Abderamane, 2012).

The distribution of chemical parameters is in homogeneous in the aquifer as such correlations between

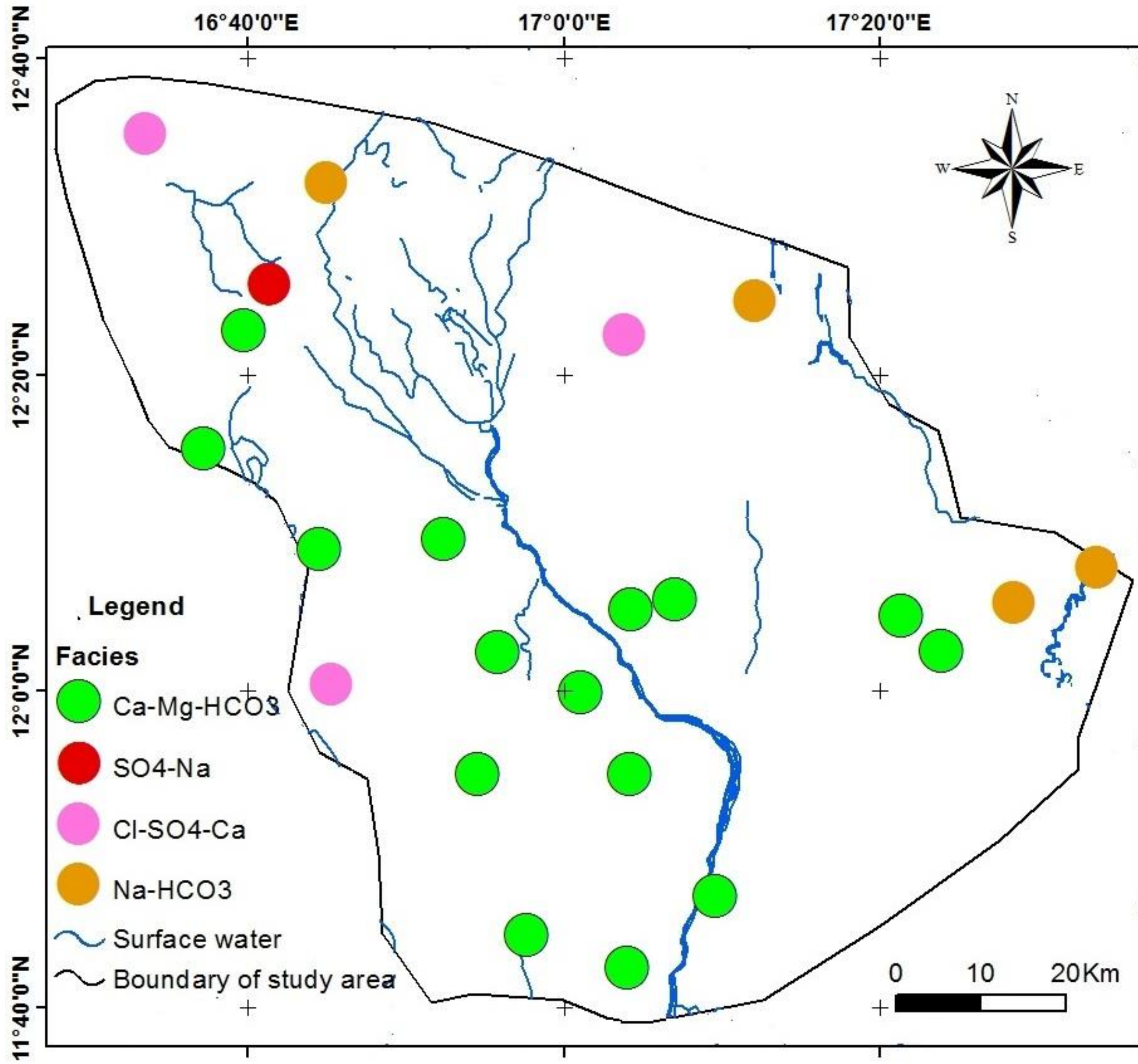

Figure 4. Spatial distribution of chemical water types in Dababa.

major ions which were determined using the Spearman correlation analysis (Table 3). A strong positive correlation (r = 0.94) was found between Na^+ and Cl^-. This high coefficient of correlation between Na^+ and Cl^- can be explained by a common origin of these ions in the groundwater. The source of bicarbonate ions in sandy aquifer derived to CO_2, engine silicate alteration reactions (Deutsch et al., 1982).The groundwater in Dababa has CO_2 partial pressure of $10^{-3.35}$ to 10^{42} higher than that of the atmosphere ($10^{-3.5}$). During the weathering of silicate minerals CO_2 is gradually converted into bicarbonate which shows positive correlation with Na^+ (r = 0.7), Mg^{2+} (r = 0.72) and Ca^{2+} (r = 0.67). There is also a positive relationship between Na+ and SO_4^{2-}, Ca^{2+} and SO_4^{2-} (Table 3). There is no correlation with the carbonate minerals in the study area. However, the combined increase of HCO_3^- and major cations could be due to the reaction between carbonic acid and silicate minerals within the sub-saturated and saturated zones of the aquifer (Stumm and Morgan, 1996). Reactions that are responsible for the release of Ca^{2+} and Na^+ which are always present in the sampled water. Carbonic acid comes from the dissolution of CO_2 by plants and micro-organisms that decompose organic matter in the soil.

The electrical conductivity is positively correlated with Ca^{2+} (r = 0.89), Na^+ (r = 0.96), Mg^{2+} (r = 0.96), HCO_3^- (r = 0.69), SO_4^{2-} (r = 0.96) and Cl^- (r = 0.96) suggesting that these elements are actively involved in the acquisition of

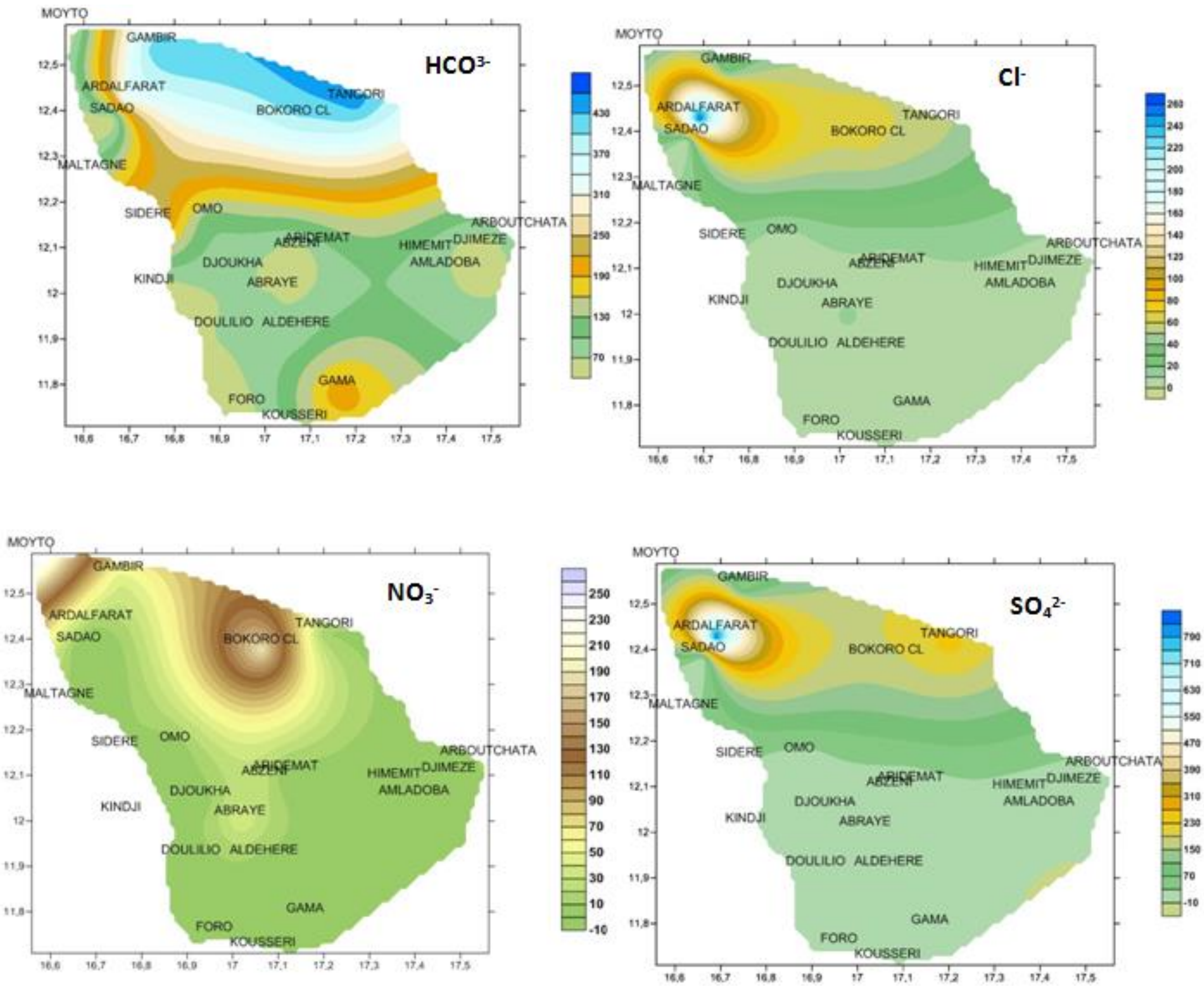

Figure 5. Spatial distribution of anions (Cl^-, SO_4^{2-}, HCO_3^- and NO_3^-) in mg/l in shallow aquifer of study area.

mineralization of the water (Abderamane, 2012). Cations and bicarbonates are from the weathering of silicate minerals in the aquifer. The porous nature of the sand causes a short residence time of water in the unsaturated zone and therefore, a minimal exchange with the bedrock explaining the observed low mineralization. Cl^- and SO_4^{2-} have not been derived from silicate weathering and generally they indicate mixtures of water from several sources.

Evaluation of groundwater quality in the Dababa area for drinking, domestic and irrigation uses; Suitability for drinking and general domestic use

In a country like Chad, where more than half of population lives in the rural areas (villages) with minimal infrastructure, with a general lack of adequate sanitation and hygiene, the concept of drinking (potable) water makes sense. The problem of drinking water is usually related to an exposure to inorganic toxic substances, heavy metals, high nitrate levels or other traces as well as bacteriological elements. However, the concentrations of chemical elements in groundwater can be natural or from pollution sources. The use of groundwater in the Dababa area for drinking and domestic use was evaluated based on the World Health Organization standards for drinking water (Table 4) (WHO, 2004). According to the work of Davis and De Wiest (1966) and Freeze and Cherry (1979) freshwater should have a TDS <600 mg/L, diluted enough to be drinkable. The EC represents the amount of total dissolved solids in the

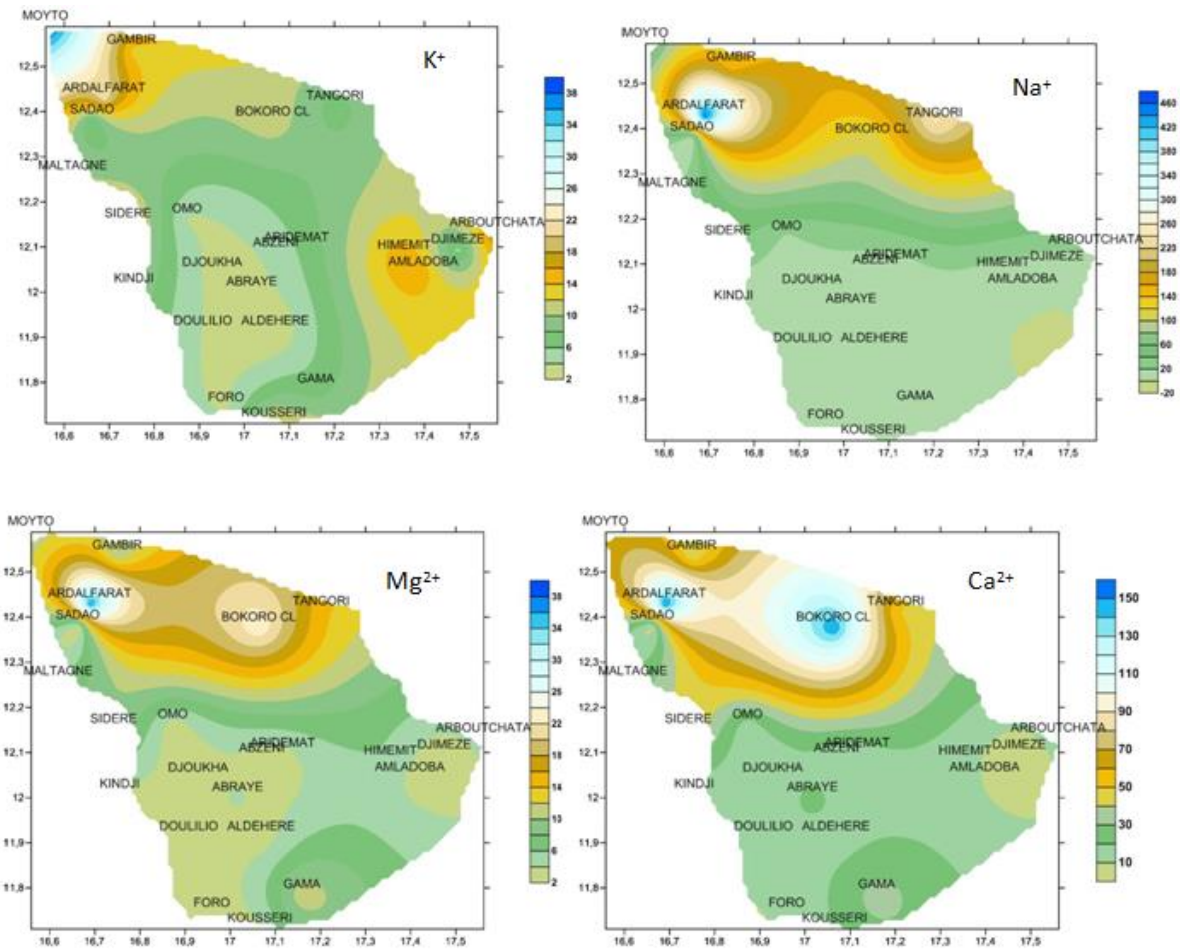

Figure 6. Spatial distribution of cations (Ca^{2+}, Na^{+}, Mg^{2+} and NO_3^-) in mg/l in shallow aquiferof study area.

water and also its inorganic filler. Only points Ardalfarat, Gambir, Tangori and Bokoro in the discharge zone near the depression, are not within the limits of 750 µS/cm. These wells are in excess of 500 mg/L TDS recommended by WHO for drinking water consumption and various domestic uses.

The pH meanwhile, has no effect on human health. It is strongly connected to the water chemical constituents. The groundwater in the study area has a pH (6.3 to 7.7) very close to the WHO range (6.5 to 8.5) for drinking water; with only 26% of the samples falling outside this limit. Hardness is an important criterion to evaluate the water for drinking, domestic and industrial uses (Karanth, 1987; Nagarajan et al., 2009). The hardness can be temporarily linked to bicarbonate and carbonate or permanently to sulphates and chlorides of Ca and Mg. Water hardness is usually expressed as the total water hardness (TH) and is expressed as follows:

$$TH = 2.5Ca^{2+} + 4.1Mg^{2+} \quad (1)$$

Where TH=total hardness in mg/L of $CaCO_3$, Ca = Ca^{2+} concentration in mg/L, Mg = Mg^{2+} concentration in mg/L (Todd, 1980). Table 5 is a presentation of the classification of groundwater in Dababa based on hardness (Durfor and Becker, 1964). About 40% of the sampled groundwater is considered hard compared to the WHO standard; while 60.87% of the groundwater in the study area can be considered soft, 17.39% moderately hard, 13.04% hard and 8.7% very hard. The problem of hard water is primarily because it does not have a good taste, it reduces the ability of soaps to foam and it causes precipitation (scaling) in pipes. The research of AkoAko et al. (2012) in the basaltic aquifers of Mount Cameroon found 44 out of 74 samples were soft and the 30 remaining moderately hard. Comparatively, waters in sedimentary terrain in Chad are less sweet. Though hardness is a parameter that depends on the geological environment and it should be noted that there is a link between water hardness and cardiovascular diseases. Dissanayake et al. (1992) found a negative

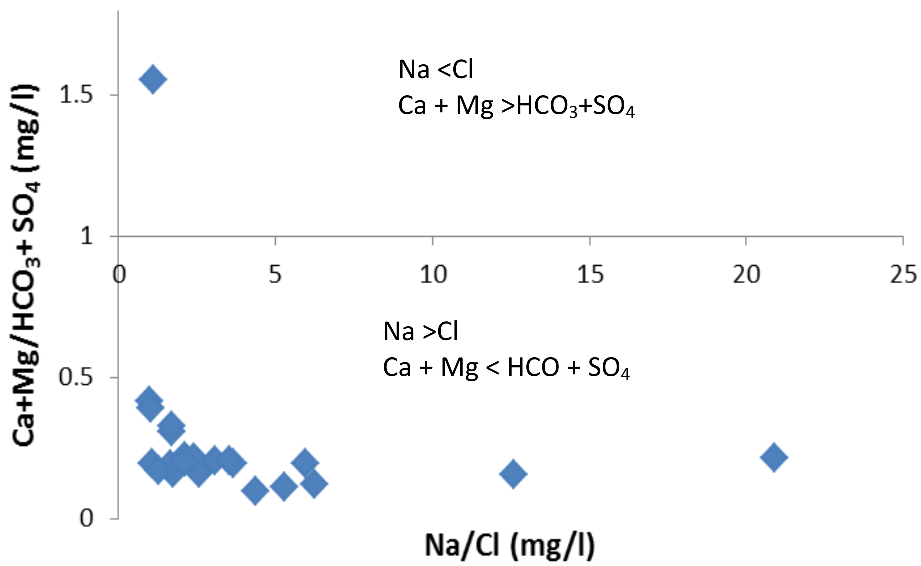

Figure 7. Relation between [(Ca + Mg) / (HCO_3 + SO_4)] and [Na/Cl], in the waters of quaternary Dababa.

Table 3. Spearman's correlation coefficients for physico-chemical and chemical parameters

Correlation	pH	EC	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3	pCO_2
pH	1										
EC	0.47	1									
Ca	0.41	**0.9**	1								
Mg	0.44	**0.97**	**0.95**	1							
Na	0.48	**0.96**	**0.76**	**0.89**	1						
K	-0.1	0.39	0.42	0.4	0.26	1					
HCO_3	0.51	**0.73**	0.67	**0.72**	**0.7**	0.09	1				
Cl	0.39	**0.95**	**0.81**	**0.91**	**0.94**	0.33	0.51	1			
SO_4	0.4	**0.94**	**0.79**	**0.9**	**0.96**	0.28	0.53	**0.99**	1		
NO_3	0.04	0.26	0.5	0.31	0.04	0.66	0.1	0.1	0.04	1	
pCO_2	-0.37	0.06	0.11	0.12	0.03	0.14	0.33	-0.02	-0.02	-0.11	1

correlation between the water hardness and the various forms of cardiovascular disease and leukemia in Sri Lanka. This implies that people consuming fresh water were more likely to suffer from cardiovascular disease than people who drink hard water. About 60% of the groundwater sampled was soft, indicating the people of this region who consume only this water have a high risk of suffering from cardiovascular problems. Magnesium was found to be one of the elements responsible for the hardness of water. On the other hand, high levels of Mg in water can make it diuretic and cathartic. Besides Ardalfarat sample, all the other points are below the permissible limit given by WHO, that is, 30 mg/L.

Sulphate ion (SO_4^{2-}) is one of the most toxic anions. The WHO (2004) recommends an upper limit of 250 mg/L. If water has a concentration of SO_4^{2-} higher than this standard, it can cause gastro-intestinal irritation resulting in a laxative effect (WHO, 1993). The sulphate values here are greater than 250 mg/L in the well of Ardalfarat. The remaining samples are below the allowable limit. After Ca, Na is the most represented cation in samples in the study area. The limit recommended by WHO for Na^+ concentrations in drinking water is 200 mg/L. High values of sodium can cause high blood pressure, heart problems, as well as kidney problems. Except in the points of Ardalfarat depression and Tangori in NE of the study area, the Na^+ and K^+ concentrations of the analyzed samples are within the

Table 4. Groundwater quality in the Dababa area and compliance to WHO (2004) drinking water standards.

Parameter	Range	Average	WHO (2004) limit	% of samples above or out of WHO guideline limit
pH	6.3-7.7	6.9	6.5-8.5	26.09
EC (µS/cm)	61-2900	474	750	17.39
Ca (mg/L)	2.31-155	33.34	75	8.7
Mg (mg/L)	2.41-37.3	7.65	30	4.35
Na (mg/L)	3.8-466	52.79	200	8.7
K (mg/L)	2.5-39.8	10.46	100	0
Cl (mg/L)	0.78-266	22.84	250	4.35
NO_3 (mg/L)	0.01-278	30.22	10	43.48
SO_4 (mg/L)	0.66-860	63.19	250	4.35
HCO_3 (mg/L)	20.8-439	144.25	200	26.09
TDS (mg/L)	54.95-2138.5	364.73	500	17.39
TH (mg/L $CaCO_3$)	15.66-540.3	114.72	100	30.43

Table 5. Hardness of spring waters in the Mount Cameroon area

Hardness (mg/L $CaCO_3$)	Water classification	Number of samples	%
0-75	Soft	14	60.87
75-150	Moderately hard	4	17.39
150-300	Hard	3	13.04
>300	Very Hard	2	8.7

Table 6. Major ion concentrations in quaternary groundwater wells. Na% indicates the suitability of water for irrigation.

Localization	K (meq/L)	Na (meq/L)	Mg (meq/L)	Ca (meq/L)	SO_4 (meq/L)	HCO_3 (meq/L)	Cl (meq/L)	Na%
MOYTO	1.02	1.03	0.85	3.21	0.56	0.34	0.59	33.54
GAMBIR	0.35	6.35	0.84	2.00	0.90	6.75	0.77	70.24
ARDALFARAT	0.54	20.26	3.11	7.75	17.92	5.30	7.46	65.71
SADAO	0.15	0.17	0.21	0.30	0.02	0.73	0.06	38.35
TANGORI	0.18	10.61	1.22	2.58	5.13	7.20	1.57	74.00
BOKORO CL	0.29	4.65	1.98	7.50	3.69	6.41	1.78	34.28
MALTAGNE	0.27	1.00	0.55	1.26	0.46	2.15	0.31	41.45
OMO	0.10	0.74	0.24	0.72	0.07	1.77	0.04	46.61
KINDJI	0.25	0.27	0.29	0.66	0.11	0.56	0.18	35.86
DJOUKHA	0.09	0.38	0.28	0.60	0.01	1.29	0.04	34.53
SIDERE	0.36	1.82	0.88	2.54	0.49	4.52	0.38	38.94
ARIDEMAT	0.16	0.40	0.27	0.69	0.02	1.42	0.07	36.51
ARBOUTCHATA	0.50	0.93	0.42	0.76	0.30	1.79	0.24	55.11
HIMEMIT	0.41	0.29	0.47	0.64	0.17	1.43	0.17	38.42
AMLADOBA	0.39	0.25	0.29	0.48	0.01	1.25	0.12	45.12
ALDEHERE	0.06	0.62	0.24	0.75	0.15	1.31	0.11	41.11
DOULILIO	0.10	0.40	0.25	0.74	0.07	1.26	0.12	33.86
FORO	0.09	0.30	0.22	0.53	0.04	0.98	0.08	34.72
GAMA	0.18	0.71	0.96	1.74	0.02	3.49	0.02	24.80
KOUSSERI	0.33	0.52	0.30	1.03	0.06	1.95	0.16	39.06
ABZENI	0.12	0.30	0.25	0.61	0.03	0.73	0.12	33.33
ABRAYE	0.09	0.56	0.36	1.20	0.04	1.16	0.35	29.39
DJIMEZE	0.13	0.23	0.20	0.12	0.03	0.61	0.02	53.31

Na% indicates the suitability of water for irrigation.

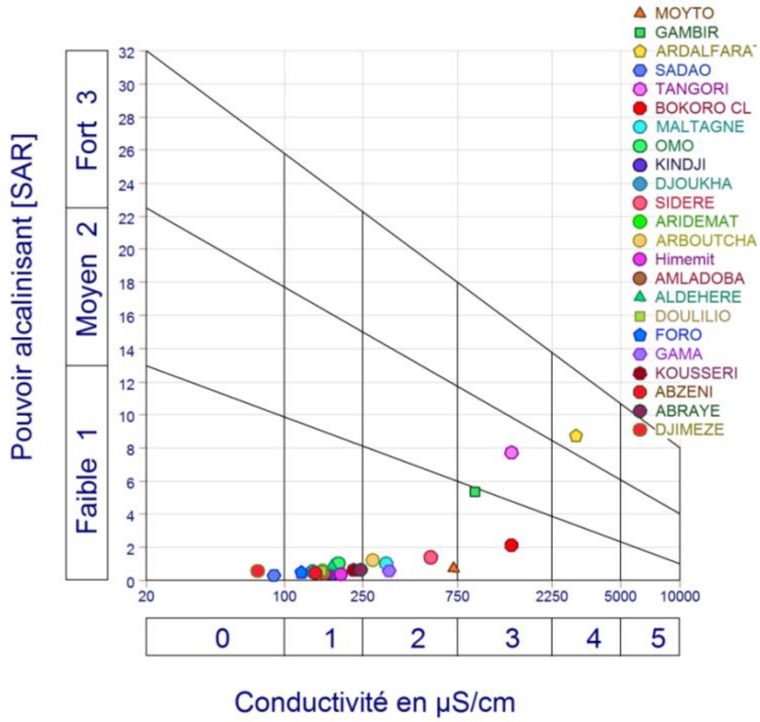

Figure 8. Diagram for classification of irrigation water according to the SAR.

limits prescribed by WHO. About 43% of samples had nitrate (NO_3^-) concentrations above the limit (10 mg/L) recommended by WHO. High nitrate contents constitute a potential danger when using the polluted resource as drinking water and consumption may generate the methomoglobine in children and cancerogenic diseases in adults (Ladouche et al., 2003).

Irrigational suitability

Water for the irrigation of plants in the study area is provided by pumping of the groundwater (wells and boreholes) and/or the use of flood waters of Batha de Lairi River. The quality of the water used for irrigation is evaluated using several methods. For the purpose of this study, we applied the classification of the United States Salinity Laboratory (1954), which is based on the sodium adsorption ratio (SAR) and electrical conductivity (EC). When sodium concentration is too high in irrigation waters, it tends to be absorbed by the clay particles in exchange for Mg and Ca ions. Sodium exchange process in the soil reduces the permeability and the result in less porous soils with low draining power. The sodium percentage of groundwater is calculated by using the following equation:

$$\% Na^+ = Na^+ + K^+/(Ca^{2+} + Mg^{2+} + K^+ + Na^+) \times 100 \quad (2)$$

Compared with the standard values, the maximum allowable concentration of Na^+ in groundwater for irrigation is 60%. The sodium percentage calculated for the shallow groundwater of Dababa varies between 24.80 and 74% (Table 2). Table 6 shows that sampled wells of Tangori, Gambir and Ardalfarat are above the norm. The proposed US Salinity Laboratory diagram, a plot of SAR values versus the EC values, is commonly used to assess the suitability of groundwater for irrigation purpose. The sodium adsorption ratio (SAR) is an important parameter for determining the suitability of groundwater for irrigation because it is a measure of risk of alkalinising cultures. It is derived from:

$$SAR = Na^+ + / [(Ca^{2+} + Mg^{2+})] \, 0.5 \text{ meq/L} \quad (3)$$

The calculated value of the SAR in the study area ranges from 0.33 to 9.18 (Table 2). The electrical conductivity (EC) is also a good indicator of the risk of salinization. High EC will to reduce the osmotic activity or the ability of plants to absorb water and nutrients from the soil. Figure 8 shows a display of samples based on the degree of salinization. 86.95% of the groundwater has low salinity and therefore low alkalinity. 13.05% have a moderate to

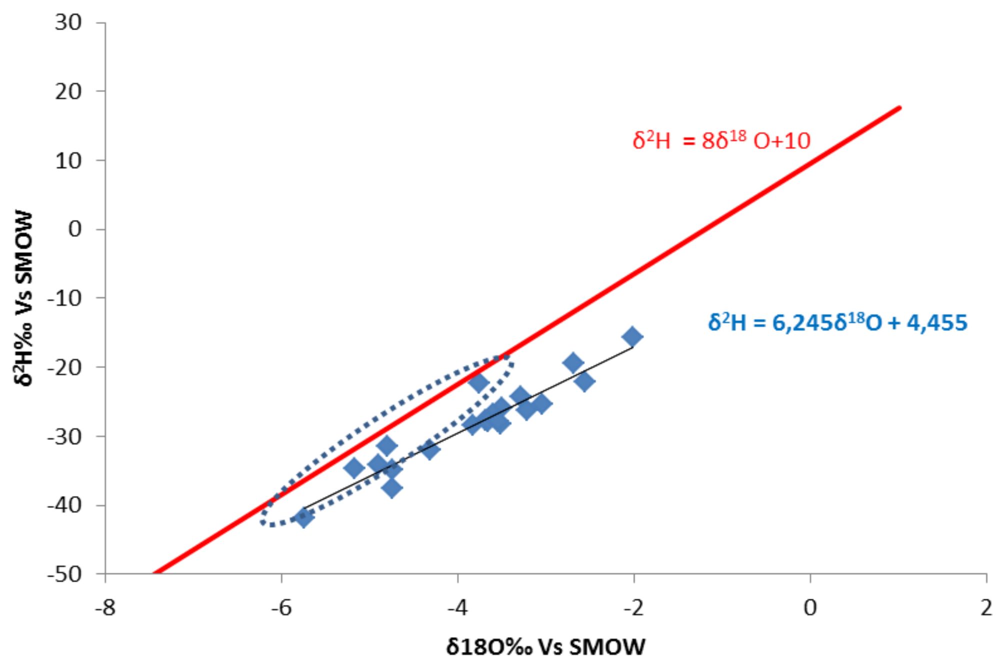

Figure 9. Relation between $\delta^{18}O$ vs. δ^2H in the waters of quaternary Dababa.

high salinity corresponding to Tangori and Ardalfarat' wells, while indicating wells that are unsuitable for irrigation.

Correlation between δ^2H and $\delta^{18}O$

The waters of the Dababa aquifer system zone show very variable isotopic content in places where the water is enriched in heavy isotopes. Thus, the deuterium values obtained lie between -41.9 and 15.7‰ vs. SMOW with an average of -28.33‰ vs. SMOW. The contents of these waters oxygen-18 varies from -5.75 to 2.01‰ vs. SMOW with an average of -3.82‰ vs. SMOW.

The whole of the deuterium and oxygen-18 values obtained had been deferred in form of graphic δ^2H vs $\delta^{18}O$ (Figure 9). On the latter, it was also deferred to the world meteoric line (DDM) of equation $\delta^2H = 8 \times \delta^{18}O + 10$ (Craig, 1961). The water evaporation line present a slope of 6.25 [$\delta^2H = 6.25\ \delta^{18}O - 4.455$] and is registered under the world meteoric line. It is noted that all the waters show a deuterium depletion and are all carried in a weak slope line as compared to the world meteoric line. This oxygen 18 enrichment in the waters indicated that it is marked by evaporation before or during the infiltration.

Thus, two (2) type of groundwater can be distinguished:

(1) The first (I) type of waters appears to be recently recharged which is located near the DMM and therefore shows isotopic signatures similar to those of rainwater which contributed to aquifer recharge.
(2) The second (II) type includes groundwater that has undergone a very significant enrichment in ^{18}O as compared to previous samples. These waters represented by the samples collected around rivers (Lake Lairi Batha and the Bahr Errigueig), deviate significantly from the DMM.

The isotopic study starting from the relation ^2H versus ^{18}O showed that the initial isotopic composition had been modified partly by evaporation of rainwater in the course of infiltration. This led to a mixture of waters of different isotopic signatures.

Conclusion

This study is the first hydro-chemical investigation in the area of Dababa located in the east-southeast of the Lake Chad Basin. The data obtained allowed us to evaluate the quality and usability of the groundwater for people living in this part of Chad (Central Africa). The groundwater in the study area is predominantly Ca-Mg HCO_3 rich. There are also Na-HCO_3, Cl-SO_4-Ca and Na-SO_4 types. The hydro-geochemical data coupled with the piezometric data reveals that water chemistry is primarily controlled by water-rock interactions and to a lesser extent by the evaporation phenomenon which mostly affects wells in piezometric depressions. The cation exchange phenomenon has been demonstrated by the diagram (Ca +

Mg)/(+ HCO_3 SO_4) versus Na/Cl. This exchange, which is facilitated by the presence of clay minerals in the geological formation, is the cause of the large variation of the concentrations of cations (Ca^{2+}, Mg^{2+} and Na^{+}) in groundwater. The waters of the studied wells appear to have an average nitrates concentration of 43.48%, which is beyond the norms for drinking water according to the World Health Organization (WHO). These results confirm the impact of agriculture and domestic wastewater discharges on groundwater. Measure to protect the groundwater, the main source of drinking water for the people is imperative. Furthermore, TH values show that the majority of groundwater is linked with the development of cardiovascular diseases. However, the Dababa groundwater can be used for irrigation, except those of the Tangori, Gambir and Ardalfarat localities in the northern part of the study area which have values of Na% 74, 70.24 and 65.71, respectively (above the 60% standard prescribed by WHO).

The isotopic study highlights that rainfall show a significant depletion in heavy isotopes. The storm origin waters evaporation are enriched in oxygen-18 and deuterium. This phenomenon leads to a specific isotopic tracing which allows to distinguish between the two types of water. In particular, we can distinguish the isotopic composition of recent water ensuring groundwater recharge through infiltration and the ancient water of the aquifer.

Conflict of Interests

The author has not declared any conflict of interests.

ACKNOWLEDGEMENTS

The authors thank the administrative authorities of the Department of Dababa (Chad) and the villagers who facilitated our access to collection points. They also like to thank the staff of the National Laboratory of Water Analysis in N'Djamena (Chad) for analyzing their water samples.

REFERENCES

Abderamane H (2012). Etude du fonctionnement hydrogéochimique du système aquifère du Chari Baguirmi. Thèse Université de Poitier, 324p.

Adams S, Titusa R, Pietersen K, Tredoux G, Harris C (2001).Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo. South Afr. J. Hydrol. 241:91-103.

AkoAko A, Shimada J, Hosono T, Kagabu M, Akoachere RA, Elambo Nkeng G, EnekeTakem G (2012). Spring water quality and usability inthe Mount Cameroon area revealed by hydrogeochemistry. Environmental Geochemistry and Health. Official J. Soc. Environ. Geochem. Health 34(5):615-639.

APHA, AWWA, WEF (1998). Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association.

Appelo CAJ, Postma D (1999). Chemical analysis of groundwater, geochemistry, groundwater and pollution. Rotterdam: Balkema.

Barbeau J, Gèse (1957). Notice explicative sur la feuille de Fort Lamy. Carte géologique de reconnaissance à l'échelle de 1/1000000. DMG, AEF, Paris 35 p.

Bellion Y (1989). Histoire Géodynamique post-paléozoïque de l'Afrique de l'Ouest d'après l'étude de quelques bassins sédimentaires (Sénégal, Taoudéni, Illumeden, Tchad). Publication occasionnelle CIFEG 19, 332 p.

Blanchot A, Muller Y (1973). Prospection de recherche minière sur la base des études géologique et des recherches antérieurs. BRGM, Paris, 142 p.

CBLT/BGR (2012). Résultats de 441 analyses chimiques des eaux souterraines et de surface dans la partie Tchadienne du Bassin du Lac-Tchad. Rapport n°4, 20 p.

CBLT/BGR (2013). Études de la qualité des eaux souterraines dans la plaine d'inondation du Logone inférieur. pp. 12-49

Coudrain-Ribstein A, Pratx B, Talbi A, Jusserand C (1998). L'évaporation des nappes phréatiques sous climat aride est-elle indépendante de la nature du sol ? C.R. Acad. Sci. Paris Sci. Terre Planète 326:159-165.

Craig H (1961b). Standards for reporting concentration of deuterium and oxygen 18 in natural waters. Science 133:1833-1834.

Dafny E, Burg A, Gvirtzman H (2006). Deduction of groundwater flow regime in a basaltic aquifer using geochemical and isotopic data: The Golan Heights. Israel case study. J. Hydrol. 330(3):506-524.

Davis SN, De Wiest RJM (1966). Hydrogeology New York: Wiley. 463 p.

Demlie M, Wohnlich S, Wisotzky F, Gizaw B (2007).Groundwater recharge, flow and hydrogeochemical evolution in a complex volcanic aquifer system, central Ethiopia. J. Hydrogeol. 15:1169-1181.

Deutsch WA, Jenne EA, Krupka KM (1982). Solubility equilibria in basalt aquifers: The Columbian Plateau, eastern Washington, USA. Chem. Geol. 36:15–34.

Dissanayake CB, Senaratne A,Weerassoriya VR (1992). Geochemistry of well water and cardiovascular diseases in SiriLanka. Int. J. Environ. Stud. 19:195-203.

Djoret D (2000). Etude de la recharge de la nappe du Chari Baguirmi (Tchad) par les méthodes chimiques et isotopiques. Thèse. Univ. Avignon, 156 p.

Durfor CN, Becker E (1964).Public water supply of the 100 largest cities in the US (Paper 1812, 364). Washington, DC: US Geological Survey Water Supply.

Freeze RA, Cherry JA (1979). Groundwater (p. 604). Englewood Cliffs: Prentice Hall.

INSEED (2012). Deuxième Recensement Général de la Population et de l'Habitat (RGPH2, 2009). 45 p.

Karanth KR (1987). Groundwater assessment, development and management.New Delhi: Tata-McGraw-Hill.

Kusnir I (1995). Géologie, ressources minérales et ressources en eau du Tchad. Travaux et documents scientifiques du Tchad. Connaissance du Tchad I. 100 p.

Ladouche B, Duvail C, Marchal JP, Le Strat P, Chery L (2003). Détermination de l'origine des nitrates dans l'aquifère du Roussillon par le traçage isotopique des sources d'azote (Commune de Pia, Pyrénées Orientales). Rapport BRGM/RP-52745-FR, 54 p.

Leblanc M (2002).Gestion des ressources en eau des grands bassins semi-aride à l'aide de la télédétection et des SIG. Application à l'étude du bassin du Lac Tchad, Afrique, université de Poitier France, 115 p.

Louis P (1970). Contribution Géophysique à la connaissance du bassin u Lac Tchad. Mém. ORSTOM N°42, 311 p.

Maurin JC, Guiraud R (1993).Basement control in the development of the early Cretaceous west and central African rift system. Tectonophysics 228:81-95.

Moussa A (2010).Les séries sédimentaires fluviatiles, lacustres et éoliennes du bassin du Tchad depuis Miocène terminale. Thèse,

Université DE STRASBOURRG, 294p.
Nagarajan R, Rajmohan N, Mahendran U, Senthamilkumar S (2009). Evaluation of groundwater quality and its suitability for drinking and agricultural use in Thanjavur city, Tamil Nadu, India. Environ Monit. Assess. 171(1-4):289-308.
Olivry JC (1986). Fleuves et rivières du Cameroun. Paris: Collection "Monographies hydrologiques Cahiers ORSTOM" ; 781 p.
Piper AM (1944). A graphic procedure in geochemical interpretation of water analysis.Transactions-American Geophysical Union 25(6):914-928.
Schneider JL (1989). Géologie et hydrogéologie de la République du Tchad. Thèse Etat Univ. Avignon 1(2):818.
Schneider JL (2001). Carte de valorisation des eaux souterraines à 1/500000. Ministère de l'environnement et de l'eau. Vol. 2 A1: 1 500 000. Document DGDH, 706 p.
Schneider JL, Wolf JP (1992). Carte géologique et carte hydrogéologique au 1/1500000 de la république du Tchad. Edition BRGM, N° 209, vol.2 et 531p.
Simler R (2007). Diagrammes. Laboratoire d'Hydrogéologie d'Avignon. Université d'Avignon. Logiciel d'hydrochimie multi langage en distribution libre.
Stumm W, Morgan JJ (1996). Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters, 3rd ed. John Wiley & Sons, Inc., New York 1022 p.
Todd DK (1980). Groundwater hydrology. New York: Wiley.
UNDP/UN (2002).Bilan diagnostic des ressources en eau : schéma directeur de l'eau et de l'assainissement du Tchad. Parti 1 document, 120 p.
United States Salinity Laboratory (1954).Diagnosis and improvement of saline and alkaline soils. Washington: US Department of Agriculture.
WHO (1993). Guidelines for drinking water quality, recommendations (2nd ed.). Geneva: World Health Organization.
WHO (2004). Guidelines for drinking water quality. Geneva: World Health Organization.